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Evidence of Corrosive Gas Formed by Radiolysis of Chloride Salts in Plutonium-Bearing Materials

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Abstract

Corrosion and pitting have been observed in headspace regions of stainless steel containers enclosing plutonium oxide/salt mixtures. These observations are consistent with the formation of a corrosive gas, probably HCl, and transport of that gas to the headspace regions of sealed containers. The NH_4Cl films found on the walls of the sealed containers is also indicative of the presence of HCl gas. Radiolysis of hydrated alkaline earth salts is the probable source of HCl.

Introduction

The US Department of Energy 3013 Standard[1] provides criteria for stabilization of plutonium-bearing materials to forms that can be packaged and placed in storage in hermetically sealed, stainless steel (SS) containers with minimal surveillance for up to 50 years. Because these materials originate from a variety of plutonium processing and disposition programs, the range of materials is extensive, ranging from nearly pure PuO_2 to impure Pu-bearing salts and compounds (PuO_2 mixed with NaCl, KCl, $MgCl_2$, $CaCl_2$ and other metal oxides). The 3013 Standard requires that, prior to packaging and storage, the materials are treated in an oxidizing atmosphere to reduce the volatile components of the stored material and to reduce the absorbed moisture to less than 0.5 weight percent. The DOE sponsored Surveillance and Monitoring Program incorporates both field and shelf-life surveillance evaluations to monitor the condition of the storage inventory and ensure long-term safe storage of 3013 containers.[2] The field surveillance activities include Non-Destructive Examination (NDE) and Destructive Examination (DE) projects currently underway at Savannah River Site (SRS). Shelf-life surveillance and material characterization are currently underway at Los Alamos National Laboratory (LANL) and Savannah River National Laboratory (SRNL) as part of the Materials Identification and Surveillance (MIS) project.

Since the inception of the Surveillance and Monitoring Program in 2003, corrosion of 300 Series stainless steels (SS), which are used as materials of construction for the 3013 containers, has been observed in both laboratory studies and in DE of 3013 containers. The corrosion is correlated with the presence of both chloride salt impurities and a relatively high humidity in the container. Corrosion has been found in both the headspace region where there is no contact between the SS and the bulk material and in the contact region where the SS is in direct contact with the bulk material. This paper specifically discusses the headspace corrosion observations and associated evidence that suggest radiolytically-produced gas-phase species may play an important role in the corrosion process(es).

Materials and Methods

The results presented here involve MIS represented materials[2], materials prepared for MIS stress corrosion cracking studies conducted at SRS[3], and observations and characterizations carried out during DE of 3013 containers at SRS[4]. The MIS represented materials reported here are named ARF-102-85-223, PMAXBS, and PEOF1. They have been characterized for elemental compositions, actinide content, density, and specific surface area[5]. The results of gas generation studies on these materials are reported elsewhere in this issue[6]. These materials were studied in either a full-scale test container or a small-scale (1:500) test container. The full-scale test container is a modified inner 3013 container made of 316L SS. The container is 4 inches in diameter and approximately 9 inches tall with internal volume of 2.3 liters. The lid is also made of 316L SS. The small-scale container is a 316L stainless steel container approximately 0.5 inches in diameter and 2.5 inches tall with internal volume of 5 mL. The container body is welded to a mini-Conflat flange and the lid is a modified mini-Conflat lid. An inner liner bucket made of 304L SS holds the plutonium-bearing material and fits snugly into the body of the small-scale test container. The details of the stress corrosion cracking studies[3] and the DE activities[4] are described elsewhere in this issue. The stress corrosion cracking observations included in this paper are from Series 4 tests[3] and the techniques used during DE include photography, scanning electron microscopy (SEM), elemental analysis of thin films and

corrosion products using energy dispersive x-ray (EDX), and crystalline phase identification using x-ray diffraction (XRD).

Results

Observations from MIS Shelf-Life Studies

As part of its mission to provide technical information to support safe storage of plutonium-bearing materials, the MIS project has conducted numerous laboratory investigations of gas generation and corrosion in sealed stainless steel test containers loaded with pure and impure plutonium oxide materials. Specimen and container exposure times ranged from months to years. Most studies have included deliberate addition of moisture up to the allowed limit of 0.5 wt.% by exposing the material to a humid atmosphere prior to sealing. Corrosion has been observed on 300 Series stainless steel (SS) container walls and test coupons when impure plutonium oxide materials containing chlorides with added moisture are sealed into the containers. These observations of corrosion include interesting differences between the headspace region where there is no contact between the SS and the bulk material and the contact region where the SS is in direct contact with the bulk material. The observed differences include a clear demarcation between headspace region and contact region (Fig. 1 a[7] and f[3]). The corrosion in the headspace region can be extensive, especially around the heat affected zone (HAZ) of welds (Fig. 1 b, c and e[3]), and the headspace region can also have broad discoloration as well as corrosion (Fig. 1 a[7], b and d). Details of the observations and analyses may be found in the referenced reports.

Surveillance Program Destructive Examination Observations

The Surveillance and Monitoring Program's DE of 3013 containers from the storage inventory has been described and a compendium of results presented in this issue.[2,4,8] One of these destructive examinations (3013 container H004111) produced several interesting observations in the headspace region that are relevant to the question of whether gas-phase corrosive species could exist in some containers. The relevant information

concerning the chemical composition of the contained material and the gas composition at the time of the evaluation is given in Table 1. The observations of the conditions of the convenience container and the inner container are:

Convenience container

1. A coating was observed on the wall of the convenience container in the headspace region but not in the region where the container wall was in contact with the plutonium bearing materials, Fig. 2 a;
2. The convenience container coating contained Cl but not Na, K, Mg,Ca, or Pu, Fig. 2 b;
3. X-ray diffraction analysis of convenience container coating detected only NH_4Cl.[4]
4. No pitting corrosion was observed under the convenience container coating.[4]
5. Pitting was observed on the convenience container lid, Fig. 2 c, and the corrosion products associated with the pit contained Cl but not Na, K, Mg, or Ca, Fig. 2 d.

Inner container

1. Corrosion was observed in an annular pattern on the inner surface of the inner container lid, Fig. 3 a.
2. Corrosion on the inner container lid includes pitting, Fig. 3 b, c and d.
3. Corrosion products associated with the pits contain Cl and the major elements found in stainless steel, but not Na, K, Mg, Ca, or Pu, Fig. 3 e.

Discussion

Pitting corrosion of stainless steel container surfaces in direct contact with salt-bearing plutonium oxide material has been observed in some cases and is thought to be due to deliquesced chlorides of magnesium and calcium, which are a minor constituent (<1%) of processing salts.[3] The relative humidity in gloveboxes during packaging of 3013 containers is too low for deliquescence of NaCl or KCl to occur.[9] Deliquescence of the alkaline earth chlorides could conceivably play a role in corrosion in the headspace regions through a dusting of small particles that will inevitably occur when handling these fine powders. However, the observations of even discoloration (Fig. 1a), corrosion

within crevices (Fig. 1c), corrosion covering large areas (Fig 1b, e and f), and extensive headspace corrosion when moisture loading is extreme (Fig. 1d) collectively suggest the participation of gas phase species may be important in the corrosion processes in the headspace regions.

The surveillance DE provides more specific evidence that HCl is the crucial species involved in the corrosion process. The detection of Cl but not the bulk salt cations Na, K, Mg, or Ca in the convenience container wall deposits, and in the corrosion pits on the convenience and inner container lids suggest that significant Cl reached the headspace surfaces in a form other than as one of the chloride salts found in the bulk material. Gas-phase HCl could plausibly be formed within the material for reasons detailed below and, because HCl is volatile, it could transport Cl to the corrosion sites in the headspace and increase the corrosion potential at these locations.

The identification of NH_4Cl deposited on the convenience container surface in the headspace region is direct evidence that both NH_3 and HCl were present in the gas phase within the container. The argument for the existence of these gaseous species is thermodynamic. Solid ammonium chloride does not sublime to molecular NH_4Cl to any significant extent, but rather sublimes dissociatively to gas-phase NH_3 and HCl through the reversible decomposition reaction

$$NH_4Cl(s) \leftrightarrows NH_3(g) + HCl(g). \qquad (1)$$

The sublimation equilibrium constant, equal to the product of the pressures of the two gases ($K_P=P_{NH3}\cdot P_{HCl}$), ranges from 6 to 730 $(ppb)^2$ between 15 and 35 °C[10] (typical headspace temperatures are below 60°C). If NH_4Cl exists in a closed system with no sources or sinks for NH_3 or HCl then each gas will have a partial pressure equal to the square root of the equilibrium constant, or 2.4 to 27 ppb over this temperature range. If either NH_3 or HCl gas are involved in other reactions within the system, their individual pressures may become unequal, but their product must still satisfy the equilibrium equation if NH_4Cl is present. Consequently, the presence of NH_4Cl guarantees that both NH_3 and HCl existed in the headspace of this container before it was opened.

The specific location of NH_4Cl as a coating on the container surface in the headspace region strongly suggests that it formed within the container from gas-phase reactants, with HCl and NH_3 being the obvious candidates. It is highly doubtful that the primary source of either gas could have been NH_4Cl that existed in the material at the time of packaging because NH_4Cl would not have survived high temperature calcination. However, there are plausible mechanisms for formation of NH_3 and HCl gases through radiolysis reactions of known constituents of the contained material.

Ammonia is formed from reactions between nitrogen and hydrogen in the gas phase.

$$N_2(g) + 3H_2(g) \rightarrow 2NH_3(g) \qquad (2)$$

The reaction when used industrially to produce ammonia typically includes a catalyst and is carried out at temperatures above 400°C and pressures above 100 atmospheres. Radiation induced ammonia formation has been observed in tritium systems[11], in laboratory experiments with gamma radiation[12] and during alpha radiation with $G(NH_3)$ of 1 (1 molecule of NH_3 formed for every 100 eV of adsorbed radiation)[13] so the formation of NH_3 could occur in the 3013 containers when N_2 and H_2 gases are present. The gases N_2 and H_2 comprise over 60% by volume of the gases observed in this container at the time of opening, Table 1. It is therefore reasonable to assume that ammonia is formed by radiolysis from the gases within the container over time.

The most likely source of HCl is the hydrolysis of alkaline earth chloride salts in the stored material. The behavior of $MgCl_2 \cdot 6H_2O$ upon heating at ambient pressure has been extensively studied.[14-17] Two final products are possible.

$$MgCl_2.6H_2O(s) \xrightarrow{\text{heat}} MgO(s) + 2HCl(g) + 5H_2O(g) \qquad (3)$$

$$MgCl_2.6H_2O(s) \xrightarrow{\text{heat}} MgCl_2(s) + 6H_2O(g) \qquad (4)$$

The intermediate products MgOHCl and $Mg(OH)_2$ proceed to MgO upon further heating and are considered as part of reaction (3) for our purposes. The chemistry is complex and the branching ratio between reaction 3 and 4 varies considerably with conditions, although reaction 3 tends to dominate. It is difficult to make anhydrous $MgCl_2$ thermally without a substantial overpressure of HCl(g).

The thermal behavior of $CaCl_2.xH_2O(s)$ (where x is 2 or 4) at ambient pressure is simpler than the thermal behavior of $MgCl_2 \cdot 6H_2O$. Hydrated calcium chloride loses all waters of hydration to form anhydrous $CaCl_2$ before the temperature is sufficiently high for detectable hydrolysis to occur. However, at elevated temperatures when water vapor is available calcium chloride solid undergoes hydrolysis to form HCl and calcium oxide.[18]

$$CaCl_2.xH_2O(s) \xrightarrow{\text{heat}} CaCl_2(s) + xH_2O(g) \quad (5)$$

$$CaCl_2(s) + H_2O(g) \xrightarrow{T>500°C} CaO(s) + 2HCl(g) \quad (6)$$

The observation of HCl during TGA/FTIR determination of water in samples from material post calcination is attributed to reaction (3) and/or (6).[19-20]

The radiolysis products from gamma (γ) and alpha (α) irradiation of $CaCl_2.2H_2O(s)$, $CaCl_2.6H_2O(s)$, $MgCl_2.2H_2O(s)$ and $MgCl_2.6H_2O(s)$ have been studied.[21-22] Hydrogen is found in the gas phase. Neither study had the experimental capability to observe either $Cl_2(g)$ or HCl(g), however, in the γ radiolysis of $CaCl_2$ with low water loadings some Cl_2 was observed trapped in the solid.

The chemistry of the alkaline earth chlorides supports the possibility of formation of HCl during α radiolysis, but in studies of the radiolysis of these salts no attempt to observe HCl has been conducted because it is extremely reactive and difficult to detect. In shelf-life studies, pH paper was used to assess the possibility of an acidic atmosphere above plutonium oxide materials that contained hydrated alkaline earth chlorides. The pH paper showed an acidic environment and registered pH values between 1 and 4.

The NH_4Cl deposit on the convenience container wall of H004111 appears to be significantly thicker immediately above the material than higher in the headspace. This indicates that at the time the deposition occurred the concentration of NH_3 , HCl, or both gases was higher near the material surface than at the top of the headspace region. This is consistent with the formation of one or both gases within or very close to the material bed

and subsequent diffusion to other regions where only depletion reactions can occur. The ammonia, if formed by α radiolysis of the N_2 and H_2 gases present, will be formed within and up to 1 to 2 cm from the top of the material. The hydrochloric acid, if formed by α radiolysis of the alkaline earth chlorides present, will be formed within the material.

In this hypothesis HCl and NH_3 are produced by independent reactions from different reactants so one gas will almost certainly be in excess after NH_4Cl condensation proceeds to equilibrium. The gas in excess would be free to diffuse higher up in the headspace of the convenience container and diffuse through the filter and into the inner container, where it could then interact with the inner container lid. The existence of pitting and associated chloride corrosion products on the inner container lid suggests that HCl is the gas produced in excess in this particular container.

Water vapor and the relative humidity inside the sealed container also play important roles in gas generation/corrosion process [3]. The relative humidity within this container at the time of opening has been determined to be 11%.[9] At this relative humidity, the water and HCl vapor present within the container may condense sufficiently in the colder portions of the container to react and form the pits that are observed on the inner container lid. These pitted regions are the areas that are most accessible to vapors coming through the filter and that region should be colder than the side wall of the container [3]. The annular corroded region seen in Figure 3 (a) should also be cooler than the rest of the lid.

Pitting is observed within this container on the lids of the convenience and inner containers and not on the walls. It is possible that material surface properties of the walls are different than material surface properties of the lids. The bodies of the inner and convenience container are flow-formed and the lids are plate machined to size.[23] The machining operations, which include cutting to remove metal, significantly work hardens a volume of metal immediately beneath the machined surface by cold work. The depth of this work-hardened layer depends on machining variables including tool sharpness, depth of cut, cutting rate and nature of surface lubrication. Microhardness measurements on

cross sections from machined surfaces of 300 series austenitic stainless steels have shown that the work hardened layer beneath the surface may extend 0.25 mm into the metal.[24] Types 304 and 304L stainless steels are very prone to surface hardening because these steels partially transform to martensitic phases during room temperature plastic deformation. Alpha prime (body centered cubic) and epsilon (hexagonal close packed) martensite phases are generally both formed.[25] This highly deformed surface layer is very susceptible to pitting and can serve as an initiation site for stress corrosion cracking.[26] The characteristics of this cold worked surface layer will play a role in any surface initiated corrosion processes and will influence the observations made during the surveillance and monitoring programs. Therefore, determination of the significance of corrosion observations must include considerations of the cold worked layer on container lids and side walls.

Conclusion

The DOE 3013 Standard identifies two potential mechanisms for container degradation: internal pressurization and corrosion.[1] However, if the plutonium oxide-salt bearing material has been properly processed and stored following the DOE-STD-3013 storage standard, there are no pressurization concerns.[6] The remaining concern is the formation of localized corrosion events within the hermetically sealed containers. The conditions for corrosion are controlled by the salt phase, moisture and corresponding relative humidity inside the storage container. Ionizing radiation (alpha particles) may result in acidic gas production such as HCl in these plutonium salt environments and HCl could be a significant factor in headspace corrosion. The generation of NH_3 when N_2 and H_2 are present would lead to the generation of the weak base NH_4Cl, which has a low vapor pressure and a high deliquescence relative humidity. The ammonium chloride deposits are evidence that HCl can be present in the headspace of a container in storage. The HCl is a potential mode for gas-phase chloride transport from the convenience container to the observed corrosion sites on the inner surfaces of the inner container. Transport via HCl is consistent with the absence at the corrosion sites of salt cations originally associated with the chloride in the packaged material. However, despite the formation of an apparent

corrosive gas and the potential for corrosion in regions outside the contained material, these conditions have not led to formation of large through wall corrosion pits or stress corrosion cracking. The headspace corrosive conditions result in only small shallow pitting events that should not produce a through-wall corrosion event within a fifty year storage life.[7,27] This, in combination with an extremely robust container design will assure the ongoing safe storage of these materials within 3013 containers. These conclusions are expected to be confirmed through continuing surveillance of the 3013 storage inventory.

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5. Permalinks to the material datasheets are
ARF-102-85-223: http://permalink.lanl.gov/object/view?what=info:lanl-repo/lareport/LA-UR-09-07116
PMAXBS: http://permalink.lanl.gov/object/view?what=info:lanl-repo/lareport/LA-UR-09-07129
PEOF1: http://permalink.lanl.gov/object/view?what=info:lanl-repo/lareport/LA-UR-09-07130

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Table 1. Data from container H004111 (FY09 DE#2).

Date Inner container welded	12/3/2003
Date opened	9/30/2008
Elemental contents in weight %	
Actinides	72
Cl	5.8
Na	1.9
K	3.0
Mg	0.7
Ca	0.06
Gas compostion, vol%	
He	34
H_2	22
N_2	44
O_2	0

Figure 1. Examples of differences between headspace region corrosion and contact region corrosion: (a) 304L inner bucket from a small-scale test container where headspace region (left of the vertical line) is characterized by discoloration and large number of small pits and contact region (right of the vertical line) is characterized by large pits on a shiny surface, material – ARF-102-85-223 (b) headspace region of fill-scale test containers showing 316L lid with HAZ and large patches of corrosion and pitting, the contact region is shiny with no corrosion, material – PMAXBS (c) lid section of a Lawrence Livermore National Laboratory inner container of 316L SS that was suspended in headspace region of a full-scale test container showing extensive corrosion in the crevice (lid section is opened for observation) between lid and wall, material – PMAXBS (d) headspace region of small-scale test container body made of 316L SS showing massive corrosion, material – PEOF1 with 5 wt% $CaCl_2$, (e) tear drop coupon of 304L that was positioned in headspace region of the corrosion tests showing extensive corrosion in heat affected zone around weld, material – Series 4 and (f) flat coupon of 304L SS from a corrosion test where the top half is in headspace region and bottom half is in contact region illustrating the boundary between them, material – Series 4.

Figure 2. Observations of the conditions on the inside surfaces of the convenience container from destructive examination of 3013 container H004111: (a) a composite of photographs of the wall, (b) EDX spectrum of the thick film, (c) SEM of a corroded region on the lid, and (d) EDX spectrum of the corrosion products associated with a pit on the lid.

Figure 3. Observations of the conditions on the inside surfaces of the inner container from destructive examination of 3013 container H004111: (a) photograph of the inner surface of the lid showing an annular pattern of corrosion, (b) SEM of the annular corroded region showing pitting pattern associated with the maching grooves, (c) SEM showing a pit with corrosion product, (d) SEM of the annular corroded region showing clustering of pits along the machining groove, and (e) EDX of corrosion product shown in (c).

Figure 1.

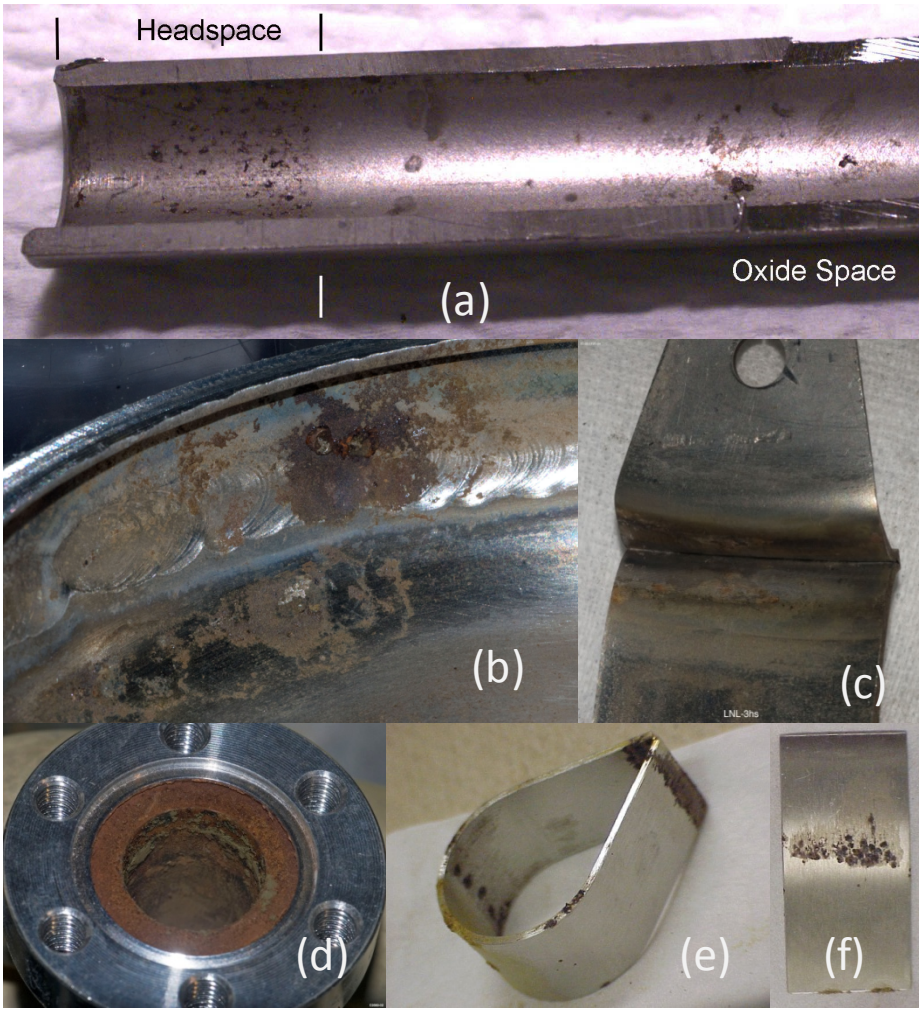


Figure 2.

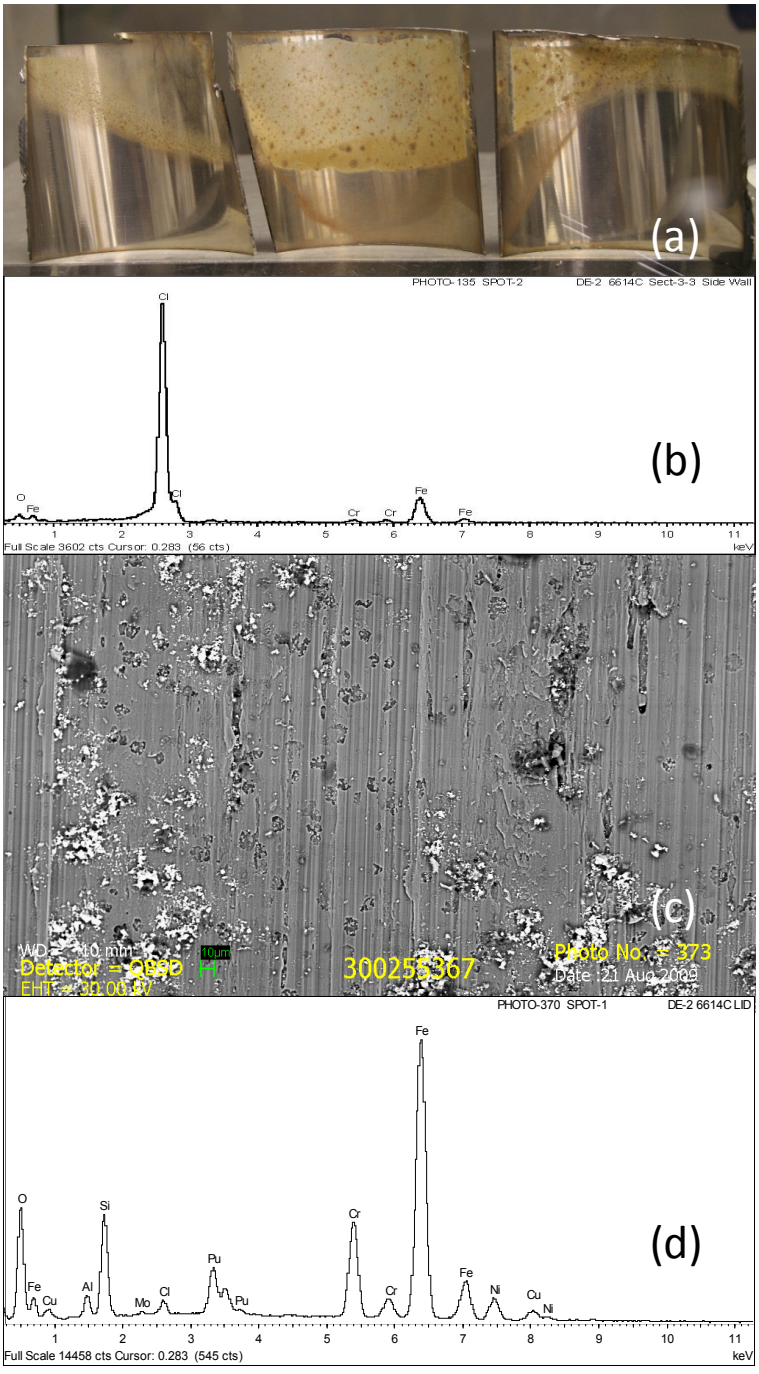
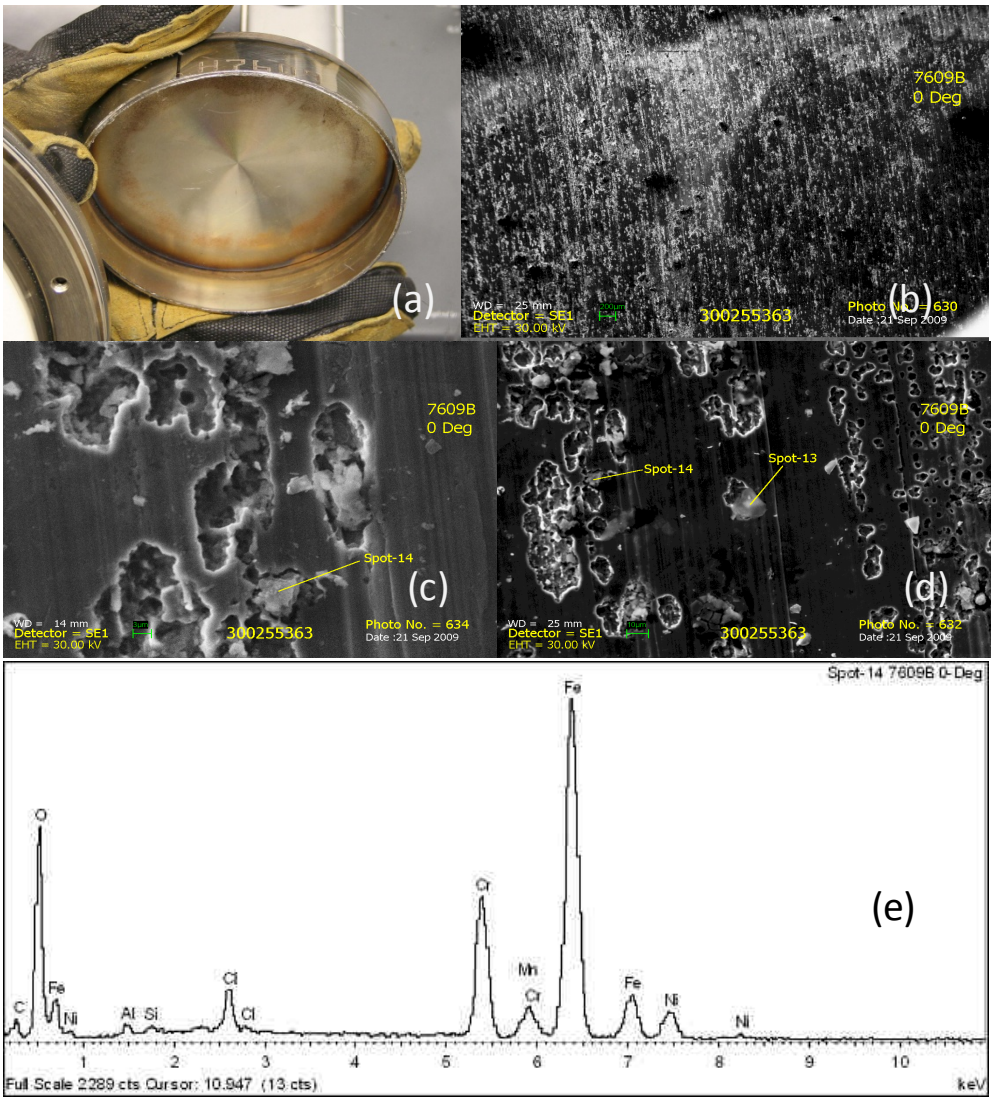

(a)
PHOTO-135 SPOT-2
DE-2 6614C Sect-3-3 Side Wall
(b)
Cl
O
Fe
Cl
Cr
Cr
Fe
Fe
Full Scale 3602 cts Cursor: 0.283 (56 cts)
keV
(c)
WD = 10 mm
Detector = QBSD
EHT = 30.00 kV
300255367
Photo No. = 373
Date :21 Aug 2009
PHOTO-370 SPOT-1
DE-2 6614C LID
(d)
O
Fe
Cu
Si
Al
Mo
Cl
Pu
Pu
Cr
Cr
Fe
Fe
Ni
Cu
Ni
Full Scale 14458 cts Cursor: 0.283 (545 cts)
keV

Figure 3


(a)
7609B
0 Deg
300255363
(b)
Spot-14
(c)
Spot-13
(d)
Spot-14 7609B 0-Deg
O
Fe
C
Ni
Al Si
Cl
Cr
Mn
Ni
(e)
Full Scale 2289 cts Cursor: 10.947 (13 cts)
keV